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16. ABSTRACT The paper is an overview of organic acid use to enhance the limestone flue gas desulfurization (FGD) process, and describes the application of this technology in operating FGD systems. The case studies illustrate the potential economic benefits of converting FGD systems to organic-acid-enhanced limestone scrubbing systems. Organic acids were identified as potentially attractive buffering agents for FGD systems more than 10 years ago. Use of the acids to counteract the effects of high concentrations of dissolved salts has resulted in increased SO2 removal efficiencies, lowered operating costs, decreased limestone consumption, increased system flexibility (e.g., ability to respond to unplanned fluctuations in coal sulfur content), and improved process reliability.

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JOURNAL ARTICLE

Organic acids can enhance wet limestone flue gas scrubbing

This article presents an overview of organic acid use in flue gas desulfurization (FGD) systems with case studies of actual, operating installations

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Organic acids used to enhance flue gas desulfurization (FGD) systems can reduce operating costs and increase SO_2 removal rates.

Organic acids were identified as potentially attractive buffering agents 10 years ago. Used to counteract the effects of high dissolved salts concentrations in FGD systems, they have increased SO_2 removal efficiencies, lowered operating costs, decreased limestone consumption, increased system flexibility (the ability to respond to fluctuations in coal sulfur content), and improved process reliability.

Adding an organic acid to a limestone FGD system increases the capacity of the slurry liquid to absorb SO_2 by buffering the pH in the absorber.

These reactions take place:

Sulfur dioxide + water = acidity (H^+) + sulfites (1)

Organic buffer anion (carboxylate ion) + acidity (H^+) = organic acid (2)

As the buffer reacts with the acidity formed in the SO_2 absorption reaction, a weak organic acid is formed (Reaction 2). The buffer is regenerated in the reaction tank by adding limestone:

Organic acid + sulfites + limestone = organic buffer anion + calcium sulfite oxides + carbon dioxide (3)

Some FGD systems can meet SO_2 emission regulations only at high absorber pH levels, resulting in increased operating costs and maintenance problems. The same SO_2 emission limits can be met at lower pH levels by adding organic acids. Each scrubbing facility has its own operating conditions, and evaluation of the viability of organic acid application must be made on a

Table 1. Facilities currently using or considering the use of organic acid enhanced limestone FGD systems

Utility	Facility	Considering use	Currently using
Associated Electric Cooperative	Thomas Hill generating station, Moberly, MO		•
Big Rivers Electric Corp.	R. D. Green station, Sebree, KY	•	
Central Illinois Light Co.	Duck Creek station, Canton, IL		•
Indianapolis Power & Light	Petersburg 3, Petersburg, IN		•
San Miguel Electric Cooperative	San Miguel station, Jourdanton, TX		•
Seminole Electric Cooperative	Unit 1 and Unit 2 Palatka, FL		•
South Carolina Public Service	Cross generating station, Cross, SC	•	
Springfield City Utilities	Southwest power plant, Springfield, MO		•
Springfield Water, Light & Power	Dallman station, Springfield, IL	•	
Texas Municipal Power	Gibbons Creek, Bryan, TX	•	
Texas Utility Generating Co.	Sandow station, Rockdale, TX		•

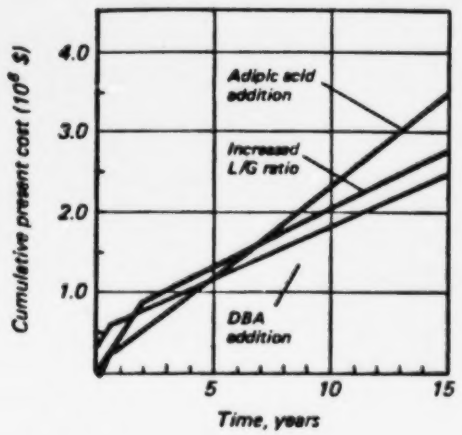

Figure 1. Cumulative present cost for Southwest power station.

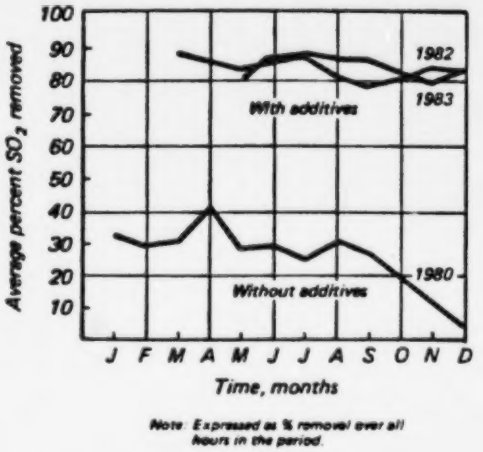

Figure 2. Comparison of Southwest power station SO_2 removal efficiencies with and without organic acid additives.

case-by-case basis. For many facilities the costs of organic acid addition may be more than offset by reduced limestone consumption.

EPA conducted an extensive research program designed to provide a thorough evaluation of various organic acid additives and how they can be used to improve lime/limestone scrubbing. The agency began by sponsoring theoretical and laboratory investigations of a number of different acids.

An organic, dibasic acid called adipic acid appeared to be the most promising because of its water solubility, low volatility, chemical stability, non-toxicity, high availability, and low cost. Also, the region for maximum buffering for adipic acid, between pH 4 and 6, is ideal for limestone FGD systems.

Two full-scale test programs were also sponsored by EPA to demonstrate technical and economic viability for utility and industrial FGD systems. The programs verified the viability of organic-acid-enhanced operations.

Since EPA's initial efforts, at least 11 utilities are considering the use of, or have converted their lime or limestone systems to, organic-acid-enhanced operations. (See Table 1.) For some utilities, the motivation for conversion is improvement of SO_2 removal efficiency. For others, organic acid enhancement is regarded purely for cost-saving.

Technical and economic analyses were made for four FGD installations to determine the nature and cost of converting each to an organic-acid-enhanced limestone scrubbing system. Three have limestone scrubbing systems: City Utilities' Southwest power plant, Central Illinois Light's Duck Creek station, and San Miguel Electric Co-op's San Miguel station. The fourth, Big Rivers Electric's R. D. Green station, has a lime-based FGD system.

Technical evaluations were made to identify any process modifications required to convert each system to an organic-acid-enhanced system and to establish organic acid makeup requirements. Capital investment costs for all required process modifications and the annual operating costs of organic-acid-enhanced operations were determined. The results for each system are summarized in the following case studies.

City Utilities (CU) was interested in improving SO_2 removal to comply with regulatory requirements. Alternatives considered included: increasing liquid-to-gas (L/G) ratio to the tray tower, adding adipic acid, and adding a mixture of organic dibasic acids (DBAs). The DBA mixture is a by-product of adipic acid production and consists of adipic, glutaric, and succinic acids.

The higher L/G option represented a capital cost intensive solution. The adipic and DBA options had lower capital costs but higher annual operating costs.

Figure 1 shows results of a present worth analysis. The adipic acid option is a lower cost option than increased L/G for about six years. The technical uncertainties in making the L/G modification, coupled with the demonstrated adipic acid system flexibility, make the adipic acid option a good choice.

However, the DBA option is the best choice, economically, through more than 15 years. Consequently, City Utilities elected to convert its FGD system to DBA-enhancement in December, 1981.

On the whole, FGD performance was enhanced to such an extent that the Southwest power plant consistently operated in compliance with the federal emission limit.

Figure 2 shows SO_2 removal efficiency by month for 1982 and 1983. (The missing 1983 data is due to a boiler outage.) It can be seen that removal efficiencies were consistently greater than the approximately 82% generally required at the plant. For comparison, Figure 2 shows performance prior to use of DBA when removal efficiencies were erratic and averaged only 26%.

DBA also increased the flexibility of the FGD system, allowing successful operation over a wide pH range. The addition of DBA also improved the system's ability to respond to operational changes. During a two-week period in March 1983, the coal burned at the plant contained 4.5% sulfur instead of the 3.5% for the which the system was designed. The unit's compliance was maintained by increasing the DBA feed to the system. The average coal sulfur content for the rest of the two-year period was 3.7%.

The overall reliability of the system was also increased significantly in 1982 and 1983 in comparison with other years. Figure 3 shows the monthly average reliability for organic acid enhanced operations compared with 1979 and 1980. The improvement may have resulted in part from DBA addition, but it was also related to a number of process improvements made during 1981 and 1982 such as the conversion from turbulent contact absorption towers to tray towers. Operation at a reduced pH, in conjunction with a better utilization of fresh water to the FGD system, al-

lowed CU to achieve an overall reliability of 97.5% in 1982 and 98.7% in 1983.

The FGD system was upgraded during a 1983 maintenance outage. A limestone classification system was added to produce a finer grind. This improved limestone utilization at a higher pH and reduced DBA consumption by 20% compared to the 1982 level. A permanent DBA feed system was also added.

As was the case at CU, Central Illinois Light Co.'s (CILCO) main interest in a conversion to organic acid was related to achieving compliance with SO_2 regulations. A second objective was to improve system reliability which averaged about 60% prior to testing. Severe mist eliminator scaling caused routine scrubber outages.

The CILCO system is significantly different from the other cases because a waste disposal pond is used for solids disposal. Since a slurry waste stream of approximately 10% solids is sent to the disposal pond, the DBA or magnesium oxide makeup requirements would be increased significantly. For this reason a process alternative was also examined which included recycle by the addition of a hydroclone to concentrate the blowdown stream to 40 weight percent solids and thus reduce the additive losses.

A present worth analysis over a 15-year period showed that the DBA options cost signficantly less than the magnesium oxide addition options, except for the case in which recycle is used to reduce the amount of scrubber blowdown sent to the waste disposal pond.

Although the process options using the hydroclone for recycle showed cost advantages, the use of a hydroclone has not been demonstrated at CILCO. Because technical uncertainties exist with this application, CILCO elected to convert to a DBA-enhanced limestone scrubbing system. It has intermittent feed controls so that DBA is added only during high load applications.

The performance of CILCO's DBA-enhanced system was evaluated approximately one year after completion of the test program. The following observations were made:

1. Compliance level SO_2 removal efficiencies were being maintained using less DBA than anticipated.

2. Limestone utilization was not as high at a given pH as it was during the previous year's testing. The tradeoffs between low pH/high DBA and high pH/low DBA operation were reviewed. Based on data collected during this evaluation, it was recommended that CILCO lower the reaction tank setpoint to 5.6 pH and increase the DBA feed rate. Savings from improved limestone utilization at the lower pH more than offset the increased DBA consumption.

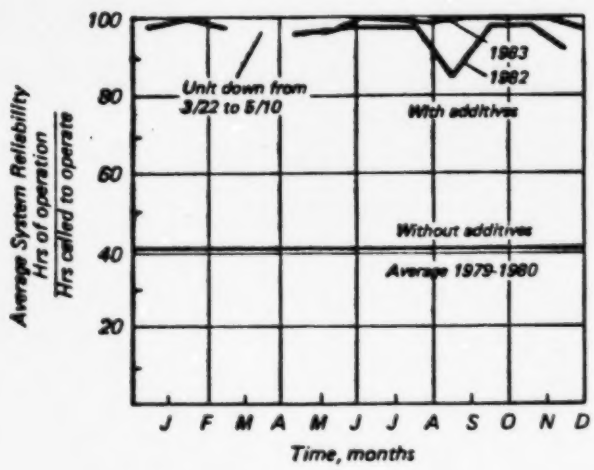

Figure 3. Comparison of Southwest power station FGD process reliability with and without organic acid additives.

Table 2. Documented 1984 cost savings

Item	Savings (costs), $1000s
Organic acid	($306)
Limestone reagent	362
Limestone grinding	37
Dewatering	16
Net savings	**$109**

Table 3. Estimated 1984 maximum cost savings

Item	Savings, $1,000
Flue gas bypass	$ 275
Reduced fan power	287
Increased high load operation	2727
Total	**$3289**

Table 4. Cost summary of first year annual costs of base case system compared with organic acid alternatives

Cost items	Base case lime system (10^6 $)	Adipic-acid-enhanced limestone system (10^6 $)	DBA-enhanced limestone system (10^6 $)
New capital investment	–	$0.898	$0.900
Alkali/additive			
Lime	$5.856	–	–
Limestone	–	1.222	1.222
Additive	–	0.931	0.418
Utilities	0.215	0.378	0.378
Total annual cost	**$6.071**	**$3.429**	**$2.918**
Annual cost savings	–	$2.642	$3.153
(mills/kWh)		0.927	1.106

3. No mist eliminator scaling or plugging was observed during the past year. The cause of the previous scaling was identified and effectively stopped by switching to a fresh water wash, adjusting the wash sequence, and improving limestone utilization by optimizing the mill circuit operation to provide a finer, more reactive product. During the testing period, the change to fresh water wash was prompted by the discovery that the wash water previously used—reclaimed disposal pond liquor—was heavily saturated with gypsum. This accounted for wash nozzle and mist eliminator header scaling and plugging.

4. FGD system reliability averaged 96% for the first half of the year and over 99% for the last half.

5. In terms of limestone consumption, the scrubbers will use almost 30 million lb/year (13.6 gigagrams) less than before. Since this limestone was passing through the scrubbers unused the waste disposal pond will see an equivalent reduction of material sent to it.

6. FGD system operating and maintenance costs dropped about 30%.

San Miguel's interest in converting to an organic acid enhanced system stemmed primarily from a desire to reduce FGD operating costs rather than from regulatory pressures.

Normal operating conditions at San Miguel required the use of fairly high limestone reagent ratios (from 1.4 to 1.6, compared to the design value of 1.2) in order to meet compliance. Besides the obvious costs associated with excess limestone use, San Miguel also experienced chemical scaling in the absorber tower which was probably related, at least in part, to the excess limestone present in the system.

In 1982 San Miguel worked with EPA to evaluate costs of converting its system to organic acid enhanced operation. The economic analysis showed that over 15 years, costs of organic acid enhanced operations could range from a $657,000 increase to a $1,550,000 savings in terms of net present worth.

The range resulted from uncertainties about the organic acid consumption rate and the estimated improvement in limestone utilization. San Miguel agreed to participate with EPA in a program to gather actual field test data at the plant to verify the results of this engineering evaluation. Included in the field test program was the evaluation of three organic acids at different concentrations in the recirculating slurry.

Taking into account the initial capital investment for the DBA system, the cost savings for the three organic acids that were tested were estimated to range from $2.9 million to $7.2 million over a 15-year period. Current operating experience indicates that this estimate was low. Note that no credit for increased reliability was assumed in any of the cost calculations.

Other potential benefits from conversion included the ability to operate the unit at higher loads and the potential for reducing station power use. Because of the expected cost savings and performance improvements associated with the use of an organic acid enhanced system, San Miquel has permanently converted its FGD system to organic acid enhanced operations.

The results of a review of San Miguel's first full year of operation with the organic acid enhanced limestone FGD system confirmed a significant reduction in operation costs. The documented savings in direct operating costs resulting from process changes made possible by the conversion more than offset acid costs. These savings are a direct result of a reduction in limestone consumption. Limestone utilization increased more than 12% over the previous year. Table 2 presents a summary of the documented cost savings.

The actual saving resulting from improved limestone utilization was $362,000, which more than offset the $306,000 cost for organic acid. An additional $53,000 savings resulted from reduced limestone grinding and dewatering costs in 1984. Other cost benefits, far outweighing the documented savings, are partly attributable to the conversion to organic acid use. An estimate of the maximum value of these additional savings is presented in Table 3.

While the portions of these benefits directly attributable to organic acid use have not been quantified, it is apparent that a significant cost savings resulted from the conversion. The ability to increase flue gas bypass and the subsequent reduction in boiler ID fan back pressure are believed to account, in part, for a shift to higher load operation. On the average, the unit operated at a 15-MW higher load in 1984. Operation at a higher average load resulted in additional revenues of $4.3 million.

Assuming that this incremental power was generated without incurring additional fixed charges, the margin on the additional power would be about 63%. As shown in Table 3, this translates the value of additional power into a cost savings of $2.7 million.

Continued operation with flue gas bypass is also believed to be responsible for the absence of scaling or plugging of the mist eliminators. Station parasitic power consumption was also reduced as a result of conversion of the FGD system to organic acid use. The total reduction for the year was estimated to be approximately 1.4 MW at full load, or about 4.5% from the previous year.

In 1982-1983 Peabody Process Systems, Inc. conducted a series of pilot plant tests at the R. D. Green station of Big Rivers Electric. A portion of these tests included comparisons of the operating costs of a lime-based FGD system to a retrofit limestone system enhanced with DBA or adipic acid. Potential cost savings from conversion of a lime system to an organic acid enhanced limestone system stem from reagent savings.

Capital cost estimates for the conversion were based on using as much existing equipment as possible. No changes to the absorption portion of the process were required. The major capital cost items were ball mills and an organic acid feed system.

A comparison of the first year operating costs of the existing lime-based system to DBA-enhanced limestone operations and adipic acid enhanced limestone operations is shown in Table 4. Results of these cost estimates indicate a first year savings of $2,642,000 for an adipic acid enhanced limestone system and $3,153,000 for a DBA-enhanced system.

The application of organic acid additives in four different FGD systems has been described. In each case, benefits were realized from the use of organic acids, including improved SO_2 removal, reliability, system performance and cost effectiveness. Although these are common goals, the approach used to incorporate organic acid enhancement varies from unit to unit. Because each facility has unique operating conditions, evaluation of organic acid must be made on a case-by-case basis.

Use of organic acid additives is one approach to improve system performance. Others, including oxidation inhibitors and modifications to system components (such as a limestone classifier, a cake dewatering system, and a mist eliminator) can be used with organic acids to optimize the system. **END**

THE AUTHORS

J. David Mobley, a senior environmental engineer at the Environmental Protection Agency, is responsible for the research, development, demonstration, and commercialization of the organic acid enhanced FGD process.

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